

Chapter 2

HUMIDITY-DEPENDENT WETTING PROPERTIES OF HIGH HYSTERESIS SURFACES

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2.1 Introduction

Microfluidic devices relying on surface forces for actuation are particularly dependent on the contact angles of the device surfaces.¹ The contact angle, θ , is the angle between the surface and the tangent to the liquid-vapor interface at the contact line. The advancing contact angle, θ_{adv} , is the contact angle measured after the contact line has moved onto a portion of the surface that has yet to be wet by the liquid. The receding contact angle, θ_{rec} , is the contact angle measured after the contact line has moved backwards from a portion of the surface that has already been wet.

Surfaces with wetting properties that change in response to stimuli have been developed in recent years for their possible utility in constructing novel devices. A full monolayer of a non-switchable molecule only allows access to a single contact angle, while responsive surfaces allow the wettability to be tuned over a range of values by varying the external

stimuli. Surfaces have been made upon which the contact angle of water changes in response to such stimuli as light,²⁻⁵ electrical potential,^{6, 7} or temperature.⁸ In most cases, however, the change in contact angle of switchable surfaces has been limited: the advancing contact angle (θ_{adv}) of water on azobenzene functionalized surfaces, for example, increased only eight degrees with UV light illumination;² and the response of a terminally charged, loosely packed self-assembled monolayers (SAM) to an electric field was limited to a change in the receding contact angle (θ_{rec}) alone.⁶

Here we examine the potential for using composition of the vapor phase to alter the wetting characteristics of a surface. In particular, we show that large changes in θ_{adv} can be induced by changing relative humidity (RH) using a surface material that has two key traits: mobility and a composition incorporating components of drastically different hydrophobicity.⁹ To facilitate drastic structural rearrangements of the surface material, a promising approach is to use physical rather than covalent bonds.¹⁰ Our lab has studied the phase behavior, dynamics, and practical application of telechelic poly(ethylene glycol) (PEG) end-functionalized with fluoroalkyl groups (R_f -PEG).¹¹⁻¹⁷ The relative lengths of the polymer midblock and the endgroups determine the phase behavior of the polymers in aqueous media: single phase gel, single phase micellar solution, coexisting gel and micellar solution, or an insoluble hydrogel. Previous work has shown that a 6 kg/mol PEG molecule with 10 fluorinated carbons (termed 6KC10) when dip coated from ethanol onto a surface premodified with a fluorinated SAM yields an insoluble gel layer that is impervious to decay at high shear rates in water. We now explore the wetting characteristics of these 6KC10 surfaces because they contain both the mobility and the diversity of wettability ideal for creating humidity-responsive surfaces.

Use of RH to alter the contact angle of water on a hydrogel has been examined by Yasuda and coworkers, who found that the surfaces became more strongly wetting with increased RH.¹⁸ As RH increased from 28% to 90%, θ_{adv} on a collagen hydrogel decreased from 90° to 75°, and on agar θ_{adv} decreased from 34° to 22°. In contrast with the work of Yasuda, we find that 6KC10 films show the counter-intuitive property of becoming more hydrophobic at higher humidity. We will argue that this dramatic

difference in behavior results from a reorganization of groups displayed at the gel surface in our materials in contrast to a change in polymer concentration in the work of Yasuda.

Reorganization of chemical groups displayed on polymer surfaces by exposure to solvents has been used to change the contact angle of water.^{9, 19} These rearrangements lower the total energy of the interface: in polar solvents groups capable of dipole-dipole or hydrogen bonding interactions move toward the surface due to their favorable interactions with the solvent. In nonpolar solvents, these groups become buried and the surface is dominated by low-energy components. Large changes in θ_{adv} can result for polymers that incorporate fluorinated moieties. Makal and Wynne synthesized a polyurethane that contained both fluorinated side groups and amide side groups in the soft block.¹⁰ Surfaces formed from dip-coating glass slides into solutions of this polyurethane showed “contraphilic” behavior: the as-formed film is partially wetting and changes to nonwetting after exposure to water. The authors ascribe the 17° increase in θ_{adv} after exposure to water to the migration of fluorinated side groups to the solid-air interface. It is hypothesized that water disrupts intrapolymer hydrogen bonds, allowing increased mobility of the chains.

Our work differs from that of Makal and Wynn in two important points. First, Makal and Wynn used a solvent to cause restructuring of a surface, while we use changes in the activity of the vapor phase. Restructuring under solvent is well documented; restructuring under a vapor phase is not. Secondly, the mechanism for RH-triggered increase in chain mobility is the dissolution of PEG crystallites at high RH. SAGA (scanning activity gravimetric analysis) studies of PEG have shown that at 21° C the isothermal dissolution of crystallites in 100 kg/mol PEG occurs in response to an increase in RH above 89%.²⁰ The transition from a semicrystalline material with absorbed water to a concentrated solution—termed deliquescence—occurs over a range of activities for PEG. Water is absorbed into the amorphous regions of the solid polymer for activities up to 86% RH and then dissolution of the crystallites occurs between 86% RH and 89% RH. In the presence of the fluorinated endgroups, studies of R_F-PEG films have shown similar swelling characteristics of unfunctionalized PEG occur.¹⁴ Our current work, therefore,

demonstrates how the deliquescence transition of a semicrystalline polymer can be used to “switch” wetting properties in response to changes in activity of solvent in the vapor phase.

2.2 Experimental

Materials Silicon wafers were purchased from Virginia Semiconductor (Fredericksburg, VA). 1H,1H,2H,2H perfluoro-1-dodecanol was purchased from Lancaster Synthesis (Windham, NH). Silicon tetrachloride solution, PEG, isophorone diisocyanate (IPDI), triethylamine (TEA), trichloro(perfluorooctyl)silane (TFOS), and anhydrous dichloromethane were purchased from Sigma Aldrich (St. Louis, MO). All salts and solvents were purchased from Caltech stockrooms; water used for wetting experiments was twice distilled.

Fluorinated SAMs A modified version of a published protocol²¹ was used to modify silicon wafers with fluoro-silanes. Briefly, silicon wafers cleaned in piranha solution (Piranha solution is a 3:1 mixture of concentrated sulfuric acid and 30% hydrogen peroxide. Silicon wafers are submerged in the solution immediately after mixing to take advantage of the high temperature generated by diluting the strong acid.), rinsed with deionized water, and dried in a stream of dry air were submerged in a solution of TFOS in hexane (2.5 wt%) for five minutes. The surfaces were removed and submerged in dichloromethane for 15 minutes and ethanol for approximately 30 seconds. Excess solvent was evaporated from the surface in a stream of dry air. Control experiments using argon confirmed that the air did not introduce any contaminants.

6KC10 thin films 6KC10 was synthesized by previously reported methods.¹³ A TFOS modified wafer was dip-coated in a solution of 6KC10 in ethanol (1 wt%) and subsequently submerged in a water reservoir for fifteen minutes. Water was then evaporated from the surface in a stream of dry air. As above, control experiments were performed using argon to insure that no contamination occurred due to the air.

PEG-grafted surfaces A published protocol²² was followed using PEG monomethyl ether with a nominal molecular weight of 550. Anhydrous dichloromethane was substituted for anhydrous benzene. A reaction time of 1 hour was used for the samples.

Ellipsometry A Gaertner L116C ellipsometer was used at 70° incident angle to estimate the thickness of the 6KC10 film. The index of refraction of 6KC10 was estimated based on the index of refraction of its components: fluoroalkyl groups are similar to poly(tetrafluoroethylene) ($n = 1.35$), alkyl groups in the spacer are similar to poly(ethylene) ($n = 1.55$), and PEG has $n = 1.43$. Therefore, the index of refraction is somewhere between 1.35 and 1.55; this range of n only changes the inferred thickness by 0.05 μm out of $\sim 1\mu\text{m}$.

Contact Angle Measurement Measurements were performed inside a homemade environmental chamber equipped with quartz windows for taking photographs (Figure 2.1). A rubber septum allowed for insertion of a micropipette tip into the chamber without altering the humidity. RH was maintained constant using standard salt solutions.^{23, 24} To ensure that the vapor phase in the chamber was in equilibrium with the saturated salt solution, the solution was continually stirred by means of a magnetic stir bar and a stir plate below the chamber, and the vapor phase was circulated using a CPU fan within the chamber. RH and temperature were monitored with a digital thermometer and humidity meter (Fisher Scientific). Surfaces were allowed to equilibrate in the environmental chamber for two hours before any measurements were made. This equilibration time was based on earlier experiments that showed an approximately ninety minute transient in gel swelling after a step change in humidity¹⁴. In one set of experiments, however, surfaces were first equilibrated at the highest humidity for two hours and then equilibrated at the lowest humidity for two hours before contact angle measurements were made. All images were taken with an EOS Digital Rebel XT from Canon (Lake Success, NY) equipped with a Canon MP-E 65mm F2.8 1-5x macro lens. To provide lighting, a bank of green LEDs was mounted behind the sample holder. Contact angles and drop diameter were measured using ImageJ (public domain, National Institutes of Health).

The protocol used to measure wetting on the 6KC10 and TFOS surfaces began by placing a 10 μL aliquot of water on the surface. A photograph of the drop was taken, and a second 10 μL aliquot was then added to the first (Figure 2.2, first row of images in each set). This was repeated until ten aliquots were added and the total drop volume was 100 μL . At this point water was then removed from the drop 10 μL at a time, and a photograph of the drop taken after each removal (Figure 2.2, second row of images in each set). The protocol for the PEG-functionalized surface was identical to that for the first two surfaces, but ten 2 μL aliquots were used in place of ten 10 μL aliquots due to the low contact angle (and thus large drop diameter) of water on the hydrophilic PEG.

2.3 Results

On the TFOS surfaces, θ_{adv} was insensitive to the RH at which the surfaces were equilibrated (Figure 2.3a). When aliquots are withdrawn from the drop, the contact angle hysteresis ($\Delta\theta = \theta_{adv} - \theta_{rec}$) is initially small ($\Delta\theta < 10^\circ$ as the drop volume is decreased to 60 μL), and the diameter of the drop retraces the values seen during the additive steps (Figure 2.3b). Further decrease in drop volume produced inconsistent results: sometimes $\Delta\theta$ remained small, in other runs it increased as the volume decreased. Therefore, the mean $\Delta\theta$ and its standard deviation increased as drop volume decreased from 50 to 20 μL . Pellerite and coworkers also observed poor reproducibility of water θ_{rec} on fluorinated alkylsilane SAMs.²⁵

On PEG-functionalized silicon, θ_{adv} was slightly larger at lower RH (Figure 2.3c). The average of the θ_{adv} measurements at all drop volumes is 24° at 94% RH, and 26° at 12% RH. As expected, the flatter drops (high RH) have a greater diameter at each volume, with a maximum disparity of 0.85 mm at 8 μL (Figure 2.3d). Note the drop diameter remains nearly constant as the first aliquots of water are removed from the surface, representing pinning of the drop perimeter.

In contrast to the small decrease in θ_{adv} on the PEG-functionalized surface as the RH changes from 12% to 94%, θ_{adv} on the 6KC10 surface increases from 75° to 95° over this same RH range (Figure 2.3e). When surfaces were first equilibrated for two hours at 94%RH and then equilibrated for two hours at 11%RH, θ_{adv} was $93^\circ \pm 5.6^\circ$. As aliquots are added to the drop on the surface, θ_{adv} remains nearly constant and the drop diameter steadily increases (Figure 2.3f). When aliquots are removed from the drop in the second part of the experiment the three phase contact line remains pinned, thus the drop diameter remains essentially unchanged as the drop volume decreases. To maintain the same wetted perimeter on the surface with decreasing drop volume, the contact angle steadily decreases. At the end of the experiment the final state of the drop is a thin film of water with the same diameter of the 100 μ L drop.

2.4 Discussion

With increasing RH, the increase of θ_{adv} on 6KC10 surfaces contrasts with the decrease of θ_{adv} observed by Yasuda on biopolymer hydrogel surfaces and by us on PEG-functionalized silicon. In Yasuda's work gels prepared at saturation (RH = 100%) can be expected to lose water in their outermost layer while equilibrating at lower humidities; the increase in concentration of gel at the surface increases the contact angle. We hypothesize that the humidity dependent wetting on PEG-functionalized silicon can also be explained by changes in polymer concentration: the ratio of polymer to water at the surface increases at low RH, again causing the contact angle to increase as RH decreases. Even at the lowest RH examined, θ_{adv} on 6KC10 was much higher than on grafted PEG. This indicates a substantial population of fluoroalkyl groups at the interface. The 20° increase in θ_{adv} at high humidity indicates increased migration of the fluoroalkyl groups to the interface.* Since the driving force for this migration—lowering of the gel's interfacial energy by the low-energy fluoroalkyl groups—is present at both high and low RH, a kinetic barrier must exist in the gel at low RH.

These results can be interpreted in light of previous studies of swelling of PEG and thin R_f-PEG films.^{14, 20} For 6KC8 samples, absorption of water into the film was found to increase dramatically at approximately 85% RH. Similar behavior is expected in the present polymer (6KC10), despite the difference in fluoroalkyl group (C8 versus C10): studies of 10KC8 and 10KC10 samples indicate that the midblock size, and not the endgroup size, determined the swelling characteristics of the sample. This dramatic increase in swelling at a particular RH was attributed to the dissolution of crystalline regions within the PEG. (DSC studies showed that 6KC10 was semicrystalline and that fluorinated endgroups did not prevent crystallization of low molecular weight PEG, only reduced the melting temperature by approximately 9°C.) SAGA studies on PEG give further insight into the nature of this transition.²⁰ Studies on levitated PEG particles were able to simultaneously measure swelling and scattering of the polymer particle at different humidities. Light scattering confirmed the hypothesized link between the drastic increase in swelling and dissolution of the crystallites. Here, the RH at which dramatic changes in θ_{adv} occur correlates with dissolution of the crystalline regions of the polymer and a jump in swelling (Figure 2.4). Crowe and Genzer also observed crystalline domains restricting the migration of endgroups to a polymer surface even though it was energetically favorable for the endgroups to be present at the surface.⁹ Unlike their materials, we can use the activity of water in the vapor phase to dissolve the crystalline regions: after losing the physical restraints imposed by the crystalline regions (Figure 2.5a) the fluorinated endgroups assemble into micellar cores in the interior of the gel and a fluoroalkyl layer at the air-gel interface (Figure 2.5b).[†] Once the fluoroalkyl groups populate the interface, the lowered energy of the gel surface keeps them localized there. In experiments where surfaces were first equilibrated at high RH and then equilibrated at low RH, the observed contact angles matched those of a surface equilibrated at high RH (Figure 2.6). Once the fluoroalkyl groups are organized at the interface, recrystallization of the PEG does not disrupt the surface.

Pinning of the θ_{rec} on 6KC10 surfaces is due to restructuring of the gel beneath the drop. When exposed to humid air, the 6KC10 surface is dominated by fluoroalkyl groups (Figure 2.5b). When exposed to water, however, these groups become buried and PEG

dominates the outer layer of the 6KC10 thin film (Figure 2.5c). Once wetted, the surface tends not to become dewetted due to the favorable energetic interactions between PEG and water, as manifested in the pinning of the contact line while water is removed from the drop. This effectively immobilizes the drop and also provides a bio-compatible surface that will protect any sensitive molecules in solution from non-specific adhesion on the surface.^{17, 26}

2.5 Conclusion

Fluoroalkyl groups in a R_f-PEG surface were shown by contact angle measurements to dominate the top layer of the 6KC10 thin film. A 20° increase in θ_{adv} occurs at high humidities. At first glance, this behavior is counter-intuitive, given that the water content of 6KC10 increases with increasing RH. Increasing RH to the point that PEG crystallites dissolve confers mobility to the film. The composition of the polymer—combining relatively polar chains with low-energy endgroups—confers the driving force for structural rearrangement to deliver the low-energy groups to the air-polymer interface. Because this increase in θ_{adv} swings from below 90° (partially wetting) to above 90° degrees (non-wetting), it may allow the range of accessible contact angle to be accentuated with roughening of the surface.²⁷ Significantly, once the water advances onto the R_f-PEG it generates a “bio-compatible” surface.^{17, 26} Since the wet R_f-PEG layer exposes only PEG, it would resist non-specific adhesion of biological molecules present in solution and make this material especially promising for use in microfluidic devices for biomedical assays. If an aqueous solution were forced into a channel coated with this material, ahead of the fluid column it would be prevented from advancing by the fluorocarbon surface present at the R_f-PEG/air interface and prevented from losing biomolecules to the walls of the channel by the hydrogel present at the R_f-PEG/water interface. Furthermore, the surface coating could play an active role since R_f-PEG gels can be loaded with a desired protein that diffuses out when the material contacts water,¹⁷ suggesting that 6KC10 layers might be used to store and release sensitive biomolecules within microfluidic devices.

* Changes in roughness can cause changes in contact angle without a change in surface composition. However, increased roughness causes surfaces with contact angles less than 90° to become more wetting and surfaces with contact angles greater than 90° to become less wetting. Roughness can not cause a transition from a contact angle less than 90° to a contact angle greater than 90° .²⁷ Therefore, we conclude that a change in surface composition must be occurring.

† Makal and Wynn consider the possibility that hydrogen bonds to the unusually acidic hydrogens on methylene units adjacent to perfluorinated carbons play a role in their materials. While such non-traditional hydrogen bonding²⁸ could occur with the backbone oxygens in PEG, it poses a much weaker kinetic restriction than that due to PEG crystallites. Therefore we emphasize the role of crystallite dissolution with increasing RH over the disruption of hydrogen bonding that may also occur.

Acknowledgement

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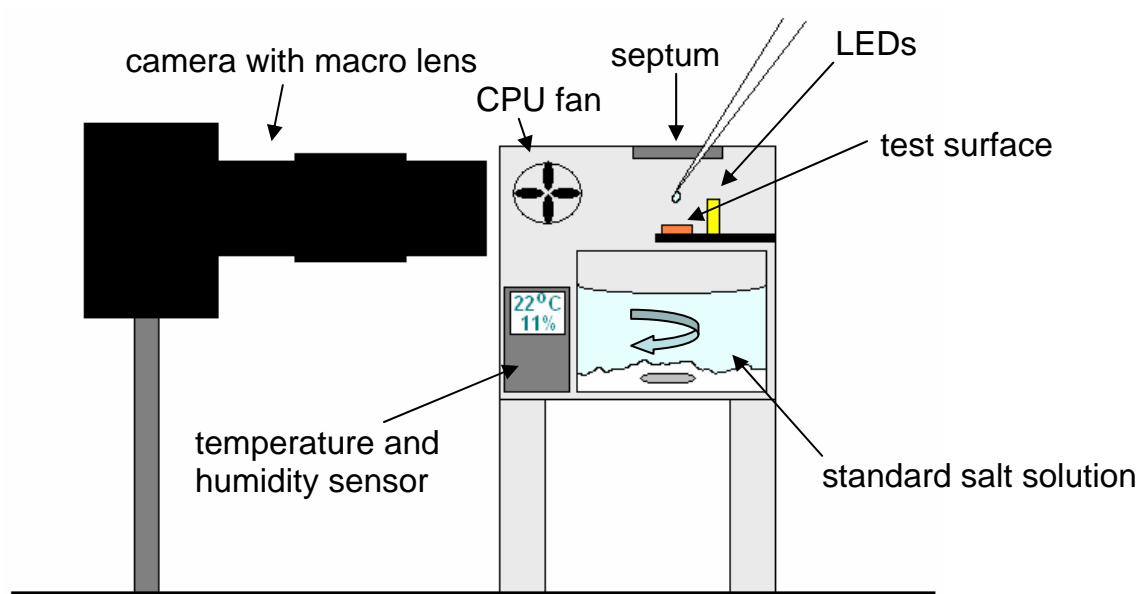


Figure 2.1 Environmental chamber for imaging drops on test surfaces(see text) that combines classical application of standard salt solutions to provide stable, precisely specified humidity with back-lit visualization of contact angle.

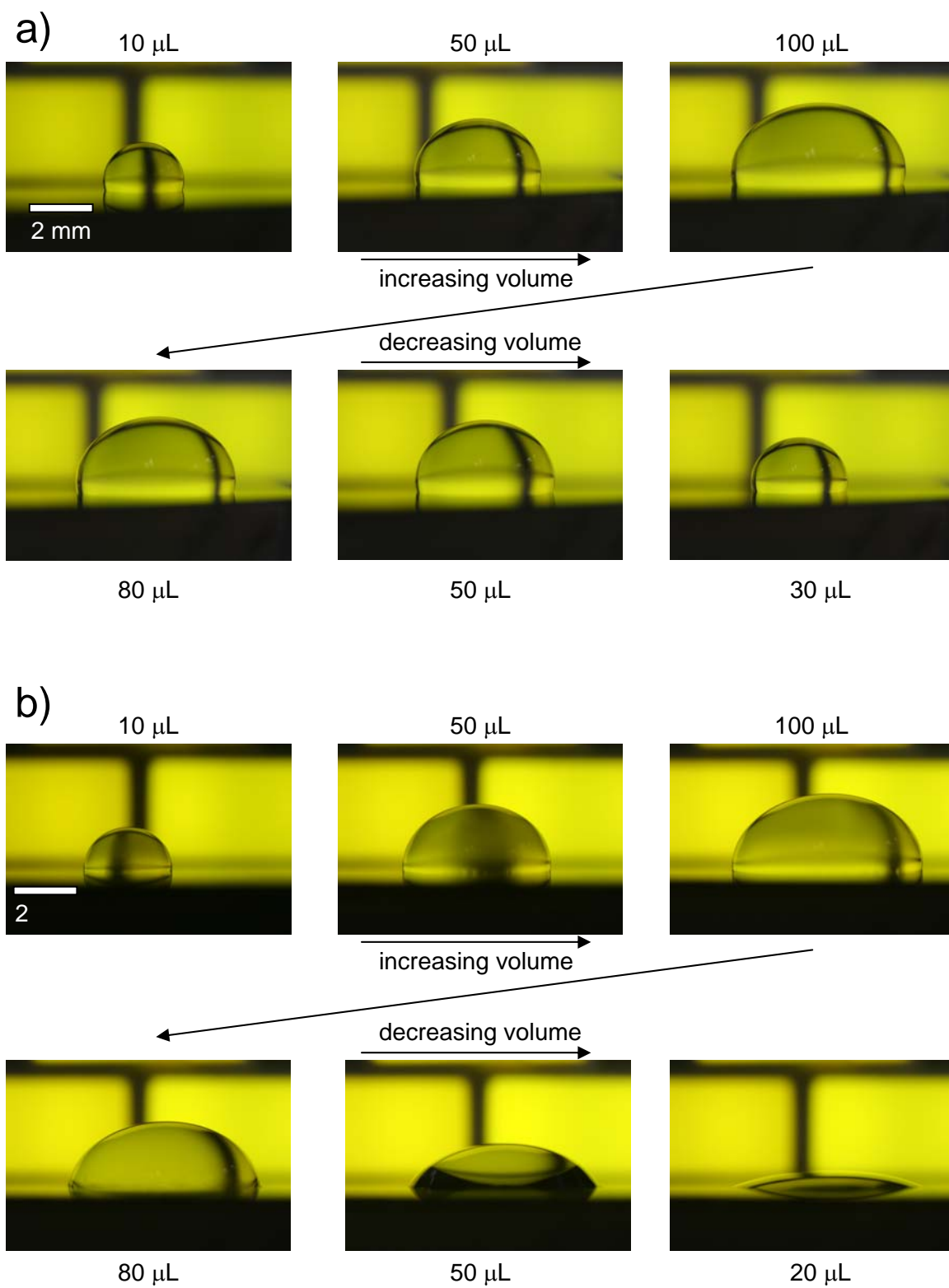


Figure 2.2 Comparison of wetting on a) a low hysteresis surface (TFOS) and b) a high hysteresis surface (6KC10). In both cases, the first three images show the advancing contact angle is high and nearly constant as the drop volume is increased. The difference in wetting behavior becomes evident when drop volume is decreased (the second row of images in each set): on the TFOS surface the contact angles remain high and nearly constant, but on the 6KC10 surface the contact angles decrease with each aliquot of water removed due to pinning of the contact line.

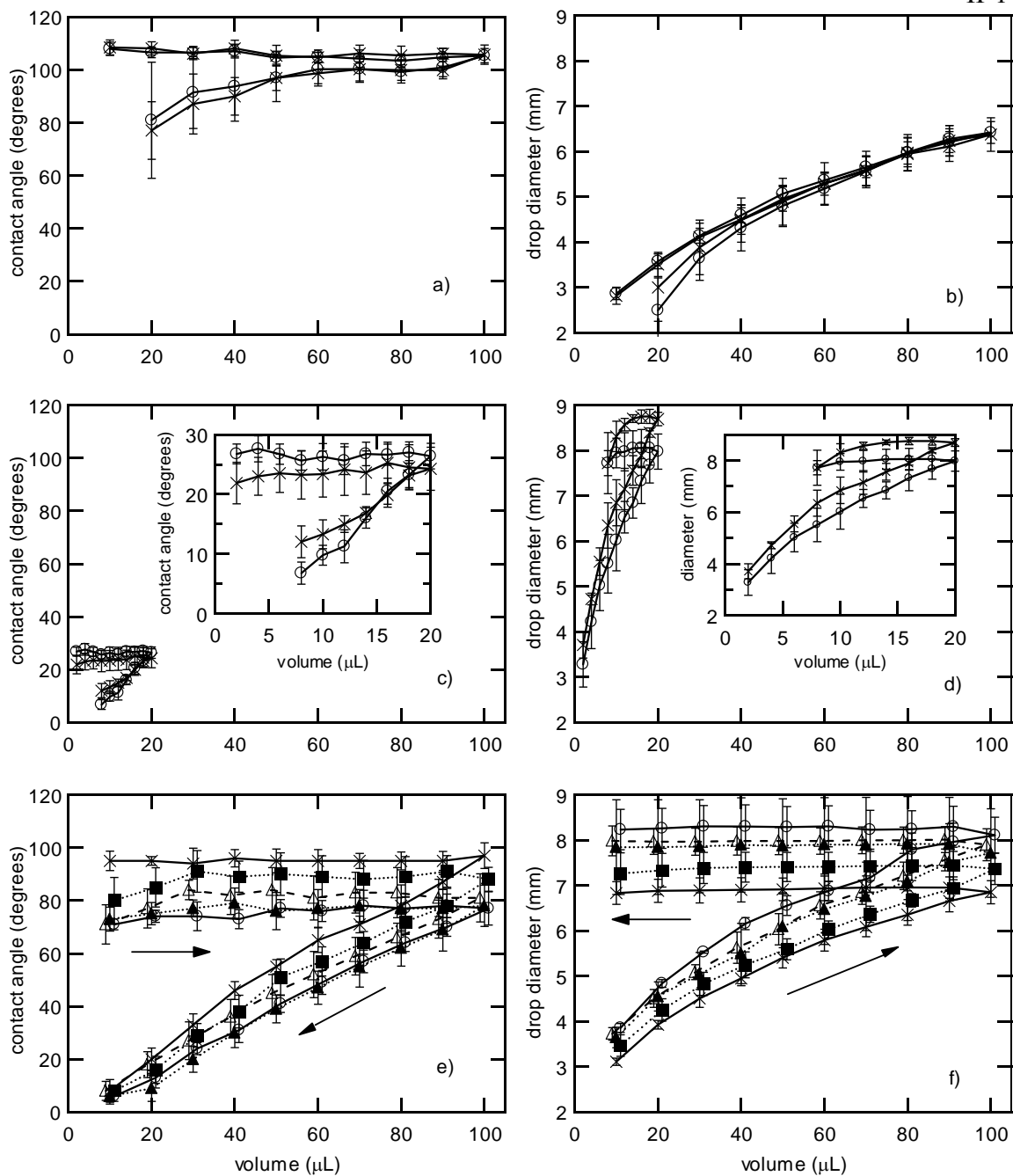


Figure 2.3 Contact angle (left) and drop diameter (right) measured during successive additions or reductions of the volume of a water drop on a given surface: fluorinated alkylsilane treated silicon (a,b), grafted PEG (c,d) and 6KC10 films (e,f). Symbols indicate the humidity at which the surface was equilibrated: 12% RH (\circ), 44% RH (\blacktriangle), 76% RH (\triangle), 84% RH (\blacksquare), and 94% RH (\times). Each reported contact angle is the average

of between eight and ten contact angle measurements, and each drop diameter is the average of four measurements. Error bars are one standard deviation.

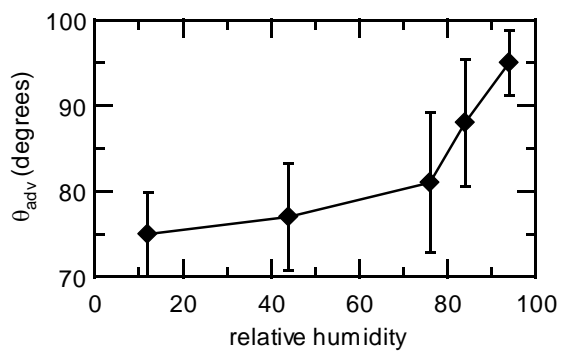


Figure 2.4 Advancing contact angles (θ_{adv}) on a 6KC10 surface as a function of the relative humidity at which the surface was equilibrated. Since θ_{adv} is insensitive to drop volume, an average was calculated using all the data collected between 10 μl and 100 μl . Error bars are one standard deviation.

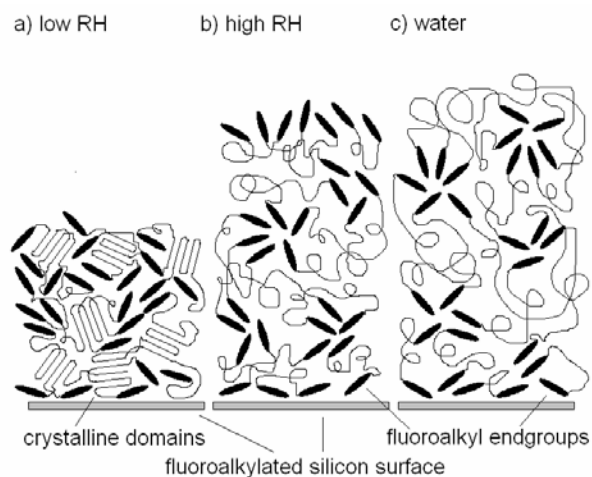


Figure 2.5 a) Schematic of 6KC10 surface exposed to dry air. Crystalline domains limit the mobility of the fluoroalkyl groups to migrate to the air interface. b) When equilibrated at higher humidities, the crystalline domains melt, the PEG swells, and fluoroalkyl groups move to the surface. c) Under water, the fluoroalkyl groups bury themselves in the 6KC10 layer, and the outer surface of the film is exclusively PEG.

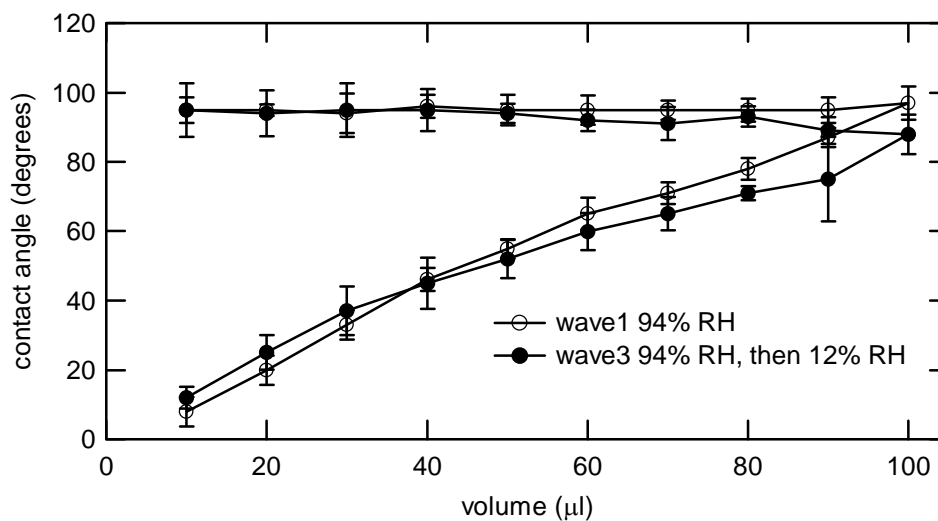


Figure 2.6 Comparison of wetting on 6KC10 surfaces that have been equilibrated at 94% RH for two hours (open symbols) with wetting on 6KC10 surfaces that have been equilibrated two hours at 94% RH and an additional two hours at 12% RH (closed symbols).

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